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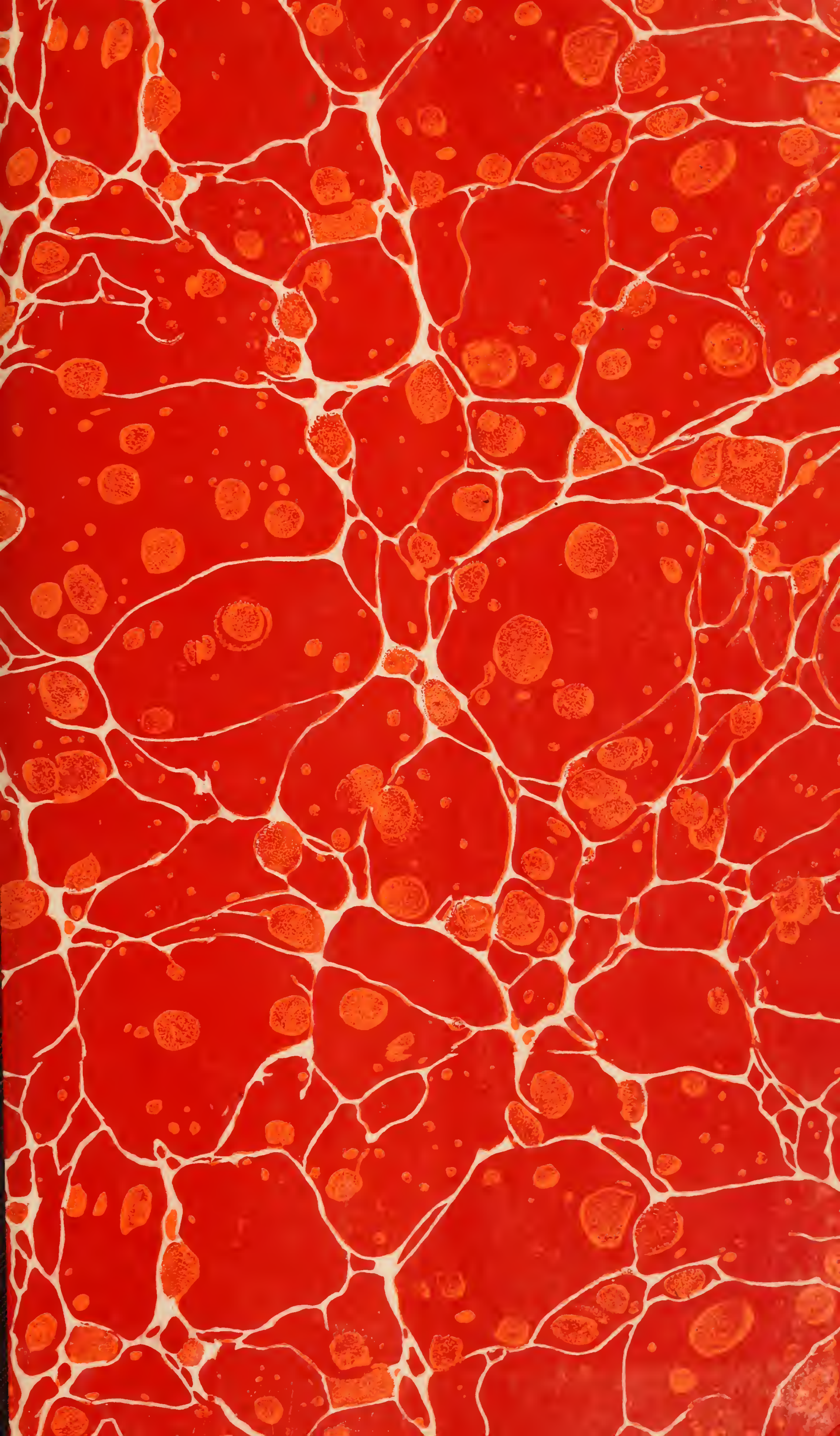

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PROBABILITIES OF RECOMBINATION INTO THE 1^2S STATE OF CAESIUM

By C. Boeckner

ABSTRACT

Measurements are made of the intensity distribution in the continuous emission band, appearing at the 1^2S series limit of caesium, using a low voltage thermionic discharge in the vapor as a source. The wave-length range covered lies between the series limit 3,184 A and about 2,750 A. The methods of photographic densitometry are employed and a tungsten strip lamp in quartz is used as a comparison source.

From the variation of intensity with wave length and the velocity distribution of the discharge electrons (obtained from probe wire measurements) are computed the relative probalities of recombination of free electrons into the 1^2S state as a function of their initial velocities. The method is that given by Mohler and Boeckner. Previous work has shown that the probability of recombination into the 2^2P and 3^2D states of caesium varies approximately inversely as the square of the velocity of the free electron, a relation which is also predicted by quantum mechanics for recombination into any level of a hydrogen atom. The present measurements show that the probability of recombination into the 1^2S caesium level falls off much more rapidly with the velocity; for electron energies greater than 0.15 volts, more nearly as the inverse fourth power.

From the probability of recombination with the emission of light, a thermodynamical relation given by Milne enables one to deduce the probability of the inverse process, namely, the absorption of light and the ejection of a photoelectron. This latter probability has been measured directly as a function of wave length by Mohler and Boeckner and by Lawrence and Edlefsen. There are some discrepancies between the measurements of these different workers. It is found, however, that the absorption wave-length curve deduced from recombination probabilities lies between the two curves obtained by direct measurement, and agrees with either within the experimental error.

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I. INTRODUCTION

The continuous emission band appearing at the head of a spectral series has been frequently observed in the laboratory.[1] It is generally ascribed to the recombination of free electrons possessing various amounts of kinetic energy into the ground level of the spectral series which it accompanies. It follows from this picture of the phenomenon that the frequency of the emitted light is given by the quantum relation

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[1] Balasse, Comptes rendus, **184**, pp. 1002 and 1320; 1927. Paschen, Berl. Ber., p. 135; 1926. Herzberg, Ann d. Physik, **84**, p. 565; 1927. Mohler, Phys. Rev., **31**, p. 187; 1928.

$$h\nu = h\nu(l) + \tfrac{1}{2} mv^2 \tag{1}$$

where ν is the frequency of the emitted quantum and $h\nu$ its energy, $\nu(l)$ the frequency of the series limit, $h\nu(l)$ the energy emitted if the electron combined from rest, and $\frac{1}{2}mv^2$ is the kinetic energy of the free electron.

It also follows that the intensity distribution in the continuous spectrum is that given by equation (2)

$$J(\lambda)d\lambda/h\nu = N^-(v).\ N.^+v.q(v).dv \tag{2}$$

The right-hand side is the number of collisions per second between electrons of velocity v and density $N^-(v)$ with ions of density N^+ (considered at rest) which results in recombination, $q(v)$ is the "effective cross section" of the ion for capture of electrons of velocity v. The left-hand side is the number of quanta radiated per second having the energy $h\nu$ and the wave length range $d\lambda$ corresponding to the velocity range dv.

It is seen from equation (2) that if measurements were made of $J(\lambda)$ and if the velocity distribution $N^-(v)$ of the electrons in the discharge tube were known it would be possible to compute relative values of $q(v)$ as a function of the electron velocity. With this end in view, Mohler and Boeckner[2] have measured the intensity distribution in the continuous spectrum appearing at the head of the 2^2P and 3^2D series of caesium. The source used was a low-voltage thermionic discharge in caesium vapor. Simultaneous measurements of the current voltage characteristics of a probe wire placed in the discharge enabled them to determine the electron velocity distribution.[3] The $q(v)$ for recombination into the 2^2P and 3^2D caesium levels which they obtained is as follows:

$$q(v) \propto \frac{1}{\nu^2 v^2} \tag{3}$$

This relation agrees essentially with that predicted by quantum mechanics for recombination into any level of a hydrogen atom.[4]

It is possible to deduce from the probability of recombination with emission of light the probability of the inverse process, namely, that of the absorption of light and the ejection of a photo-electron. The relation between these quantities (equation (4)) has been derived by Milne[5] from thermodynamical considerations and the principle of the detailed balancing of reversible events in thermodynamical equilibrium.

$$q(v) \propto K(\nu)\nu^2/v^2 \tag{4}$$

$K(\nu)$ is here the atomic absorption coefficient for wave lengths in the region of photo-electric absorption. The $K(\nu)$ for the 2^2P and

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[2] Mohler and Boeckner, B. S. Jour. Research, **2**, p. 489; 1929.

[3] According to the probe wire theory of Langmuir, the form of the characteristics obtained showed that the electrons had a Maxwellian velocity distribution.

[4] Stuekelberg and Morse, Phys. Rev., **36**, p. 16; 1930.

[5] Milne, Phil. Mag., **47**, p. 209; 1925.

3^2D states as deduced from equations (3) and (4) is given in the following equation:

$$K(\nu) \propto \nu^{-4} \tag{5}$$

The absorption coefficient in the region of continuous X-ray absorption varies as ν^{-3} as does also (approximately) the absorption coefficient derived from the quantum mechanics for the hydrogen atom.

The photo-electric absorption from the 2^2P and 3^2D caesium levels can probably never be measured. The absorption from the 1^2S level has, however, been studied quantitatively by measuring the ionization current produced by light on the short-wave length side of the 1^2S limit.[6] Although there are some discrepancies between the measurements in the two papers quoted, they both agree in giving an absorption coefficient which falls off much more rapidly with the wave length than is indicated by equation (5). The $q(v)$ deduced from the absorption coefficient falls off approximately as the inverse fourth power of the electron velocity rather than as the second power as in equation (3). It is seen, therefore, that as far as recombination or the photo-electric effect is concerned the 2^2P and 3^2D caesium levels behave like a level in the hydrogen atom, while the 1^2S level is quite anomalous.

The measurements in the present paper were undertaken with the view of ascertaining if recombination probabilities into the 1^2S level as determined directly were also anomalous and if they would be quantitatively consistent with the photo-electric experiments. It was thought that an agreement between the two types of measurements would serve as an interesting verification of the principle of detailed balance and would also confirm the various assumptions on which the method of obtaining recombination probabilities is based.

II. METHOD

1. THE DISCHARGE TUBE

A low voltage thermionic discharge in caesium vapor served as a source. The discharge tube was of silica glass with a flat window of the same material. The electrodes consisted of a cylindrical platinum anode and a concentric oxide coated platinum filament. The tube was evacuated and baked out, a small amount of caesium distilled in slowly and then sealed off from the pumps. The discharge was operated at an anode potential of 6 volts, a discharge current of 0.3 or 0.4 amperes and a caesium vapor pressure of about 0.07 mm. The latter pressure was obtained by keeping the tube at a temperature of 190° C. in a furnace.

2. THE PROBE WIRE MEASUREMENTS AND ELECTRON VELOCITY DISTRIBUTION

A small copper probe wire about 0.5 mm in diameter and 3 mm long was placed in the discharge near the point of observation. A plot of the logarithm of the electron current to the probe against the probe potential usually yields a straight line in the type of discharge used. This type of characteristic shows according to Langmuir[7] and his coworkers that the electrons have a Maxwellian velocity distribution and that the most probable energy of the electron in volts (V_0) is given by the slope of the line (if natural logarithms are used). The $N^-(v)$ of equation (2) is therefore given by the Maxwellian law of velocity distribution

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[6] Mohler and Boeckner, B. S. Jour. Research, 3, p. 303; 1929. Lawrence and Edlefsen, Phys. Rev., 34, p. 233; 1929.

[7] Mott-Smith and Langmuir, Phys. Rev., 28, p. 727; 1926.

$$N^-(v)\,d\,v \propto v^2\,\epsilon^{-\frac{1}{2}\frac{mv^2}{eV_0}}d\ v = v^2\epsilon^{-\frac{V}{V_0}}\,d\,v \qquad (6)$$

where V is the energy of the electron in volts.

Unfortunately the particular probe wire used did not give very reproducible characteristics, the values for V_0 obtained seemed to cluster about two values, namely, 0.18 and 0.22 volt. The behavior suggested that the wire was covered with an unstable caesium layer, which caused erratic variations in its contact potential.

The V_0 used, however, to compute $N^-(v)$ was obtained from measurements of the intensity distribution in the 2^2P continuous spectrum. As will be pointed out later, a plot of the number of quanta emitted per unit wave length range against the wave length expressed in volts should yield a straight line, the slope of which gives the most probable electron energy. The V_0 obtained by this method (0.22 volt) did not vary by 5 per cent during the series of measurements. This procedure was thought acceptable, since it was based on a large number of intensity and probe wire measurements in previous work.[8]

3. THE INTENSITY MEASUREMENTS

The methods of photographic densitometry were used in the intensity measurements, a tungsten strip lamp in quartz serving as the comparison source. A Hilger E_2 quartz spectrograph was used to resolve the light, and achromatic lenses to focus the discharge on the slit. Eastman 33 photographic plates were selected because of the freedom from fog and the good sensitivity. The density of the negatives was measured with a photo-electric densitometer.

The tungsten strip lamp consisted of a polished tungsten strip in an evacuated silica glass bulb with flat windows. It was calibrated in terms of its true temperature. Though the emissivity of tungsten in the ultra-violet has not been measured beyond 3,400 A, there is little doubt that its variation in the wave-length range, 4,000 to 2,750 A, is relatively small. A review of the data by Forsythe and Christison [9] indicates that the variation between the wave-length limits mentioned is only 6 per cent. The variation in emissivity with temperature is only 1 per cent between 1,800° and 2,200° K. In view of other sources of error, it seemed best to assume constant emissivity and to compute the energy radiated directly from Wien's law, using the true temperature of the tungsten.

For long exposures with the strip lamp to calibrate the plate in the ultra-violet, a bromine cell of known transmission was placed in front of the spectrograph slit. The cell absorbed most of the light between 4,500 and 3,700 A and prevented fogging.

Due to the fact that the 1^2S recombination spectrum is one hundred times weaker than 2^2P or 3^2D, it was necessary to take long exposures varying from 1 to 16 hours (depending on the spectral region measured). For the shorter exposures the discharge and the comparison source were given the same exposure times. The 16-hour exposures, however, were compared with the 4-hour exposures of the strip lamp. There was probably no error caused by the failure of the photographic reciprocity law in the latter case, since the spectral distribution curves obtained by the two procedures were consistent in the wave-length region in which they overlapped.

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[8] See footnote 2, p. 278.

[9] Forsythe and Christison, J. Opt. Soc. Am., **20**, p. 396; 1930

In the present measurements it was possible to use a simple procedure in comparing the strip lamp and the discharge exposures due to the similarity of their spectral energy distributions. Wave lengths of the recombination spectrum λ_r were found which had the same density on the photographic plate as that of the tungsten strip at some other wave length λ_t. The intensity of the discharge spectrum $J(\lambda_r)$ was then computed from the relation

$$J(\lambda_r)/D_r = J(\lambda_t)/D_t \tag{7}$$

$J(\lambda_t)$ is the intensity of the strip lamp at λ_t and D_r and D_t are the dispersions of the spectrograph at the two wave lengths. $J(\lambda_t)$ was computed from Wien's law and the true temperature of the tungsten. It was possible in this way to compute the energy distribution in the recombination spectrum by means of one or two comparison exposures. It may be remarked that the ordinary procedure of getting a large number of comparison exposures of graded intensity and thus obtaining a complete plate characteristic at each wave length would have been difficult in this work because of the long exposure times.

This method assumes that the plate sensitivity, absorption of the optical system, etc., do not change between λ_r and λ_t, an assumption which is largely correct since these two wave lengths usually differed by less than one or two hundred angstroms. Evidence for the slow change of absorption and plate sensitivity with wave length is given in the following. An inspection of the work of Harrison,[10] and Jones and Sandick [10] on the characteristics of photographic plates in the untra-violet shows that the change in energy to produce the same photographic blackening at two wave lengths is always less than 7 per cent in 100 angstroms, a change of the order of other experimental errors. Some control experiments were performed to verify these facts under the conditions of the present work. Exposures of the tungsten strip lamp were obtained at two wave lengths such that points of equal density lay about 500 A apart. It was found that relation (7) was satisfied to within an error of from 0 to 12 per cent per 100 A difference in wave length. The method outlined above was therefore considered justified.

4. THE OVERLAPPING OF THE 2^2P SPECTRUM

The most serious difficulty in the present measurements arose from the fact that the 2^2P recombination spectrum, though its limit lies at 5,000 A, has appreciable intensity at the 1^2S series limit. It was therefore necessary to subtract from the measured intensity the fraction due to the 2^2P recombination spectrum. The latter corrections were estimated by measuring the intensity distribution of the 2^2P spectrum from 4,000 A to the 1^2S limit (3,184 A) and extrapolating to shorter wave lengths. The analytical form for the intensity distribution in the 2^2P continuous spectrum can be derived from equations (2), (3), and (6). It has the following form

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[10] Harrison, J. Opt. Soc. Am., **11**, p. 341; 1925. Jones and Sandick, J. Opt. Soc. Am., **12**, p. 401; 1926.

$$\lambda \times J(\lambda) \propto \epsilon^{-\frac{V}{V_0}} \propto \epsilon^{-\frac{\overline{V}}{V_0}} \tag{8}$$

where V is the energy of the electron in volts and $\overline{V}$ is the frequency of the emitted quantum expressed in volts; that is,

$$h\nu = e\overline{V} = eV + h\nu(l)$$

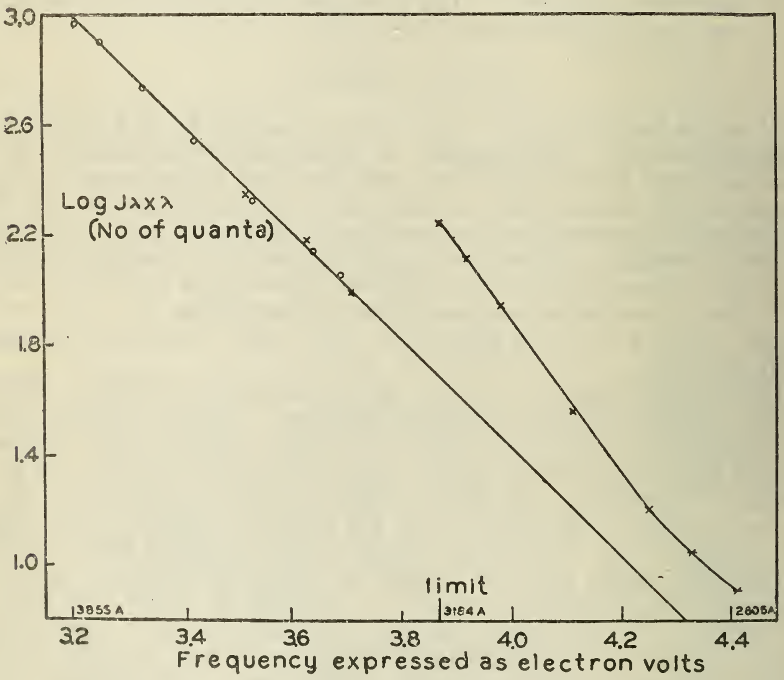

Fig. 2.—*Intensity distribution in the 2^2P and 1^2S recombination spectrum*

The extrapolation mentioned was performed by plotting log $\lambda \times J(\lambda)$ against $\overline{V}$ and producing the straight line obtained to shorter wave lengths.

It was found, however, that the overlapping was considerably reduced by taking the light from a region of the discharge tube as far from the cathode as possible. The explanation of this fact depends upon the observation [11] that the electron temperature and, therefore, the relative concentration of high-speed electrons decreases from the cathode toward the anode. The relative intensity of the recombination spectrum far from its limit should, therefore, also decrease, since it is due to the recombination of high-speed electrons.

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[11] See footnote 2, p. 278.

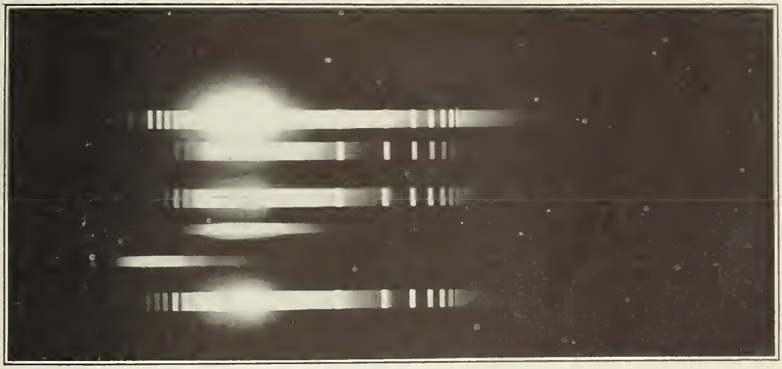

FIGURE 1.—*Typical plate, showing several exposures of the recombination spectra and of the tungsten strip lamp*

III. RESULTS

Figure 1 shows a typical spectrogram with several exposures of the caesium discharge and of the tungsten strip lamp. One sees to the left the very intense 2^2P recombination spectrum, then the lines of the 1^2S—m^2P series approaching a limit, and finally to the right the 1^2S recombination spectrum.

Figure 2 shows a plot of the intensity distribution in the continuous spectrum obtained from the measurement of a single plate. The linear nature of the plot for the 2^2P spectrum is evident as well as the nature of the extrapolation involved in estimating the intensity of the 2^2P spectrum beyond the 1^1S limit.

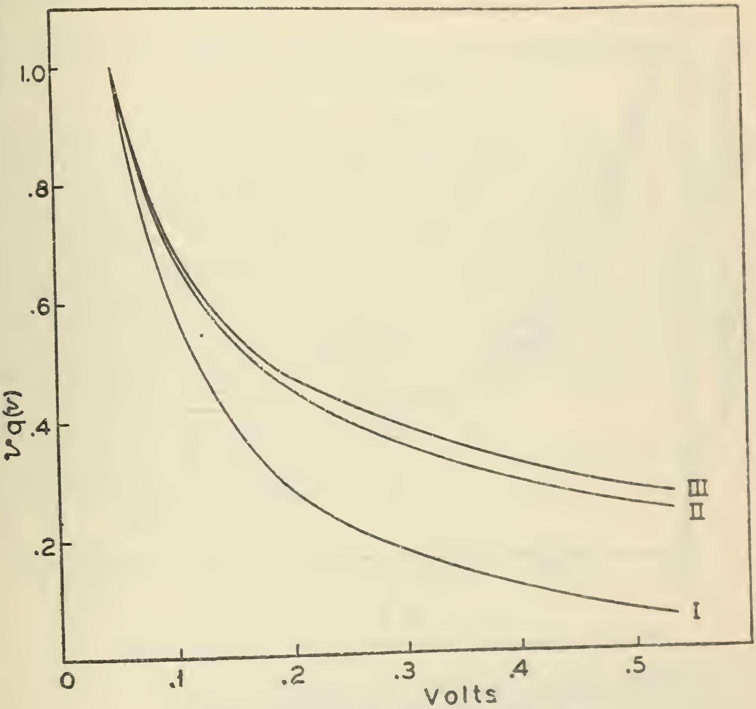

FIG. 3.—*Relative probabilities of recombination*

(Ordinates proportional to the number of collisions per second which result in recombination. The abscissa is the energy of the electron in volts.)

Curve *I*, recombination probabilities for the 1^2S caesium level.

Curve *II*, recombination probabilities for the 2^2P and 3^2D caesium levels.

Curve *III*, theoretical curve for recombination into a level of a hydrogen atom.

In Figure 3, curve *I*, are plotted the values of the recombination[2] probabilities $v\,q(v)$ computed from the intensity measurements. It is seen to fall off much more rapidly with the velocity of the electron than it does for recombination into the 2^2P level, curve *II*, or for recombination into a hydrogenlike level, curve *III*. For energies greater than 0.15 volt, $q(v)$ falls off as the fourth power of the velocity in agreement with the relation predicted by Mohler, Foote, and Chenault[12] from the measurements of the photo-electric effect.

The similar measurements of Lawrence and Edlefsen would indicate that the inverse fourth power law holds down to energies of 0.06 volt.

It can be shown, however, from equations (1) and (6) that, if the recombination spectrum intensity is to remain finite at the limit, $q(v)$ must vary as v^{-2} for very small velocities. This conclusion has also been reached by Milne by use of equation (4) and the experimental fact that the photo-electric absorption coefficient remains finite at the limit.

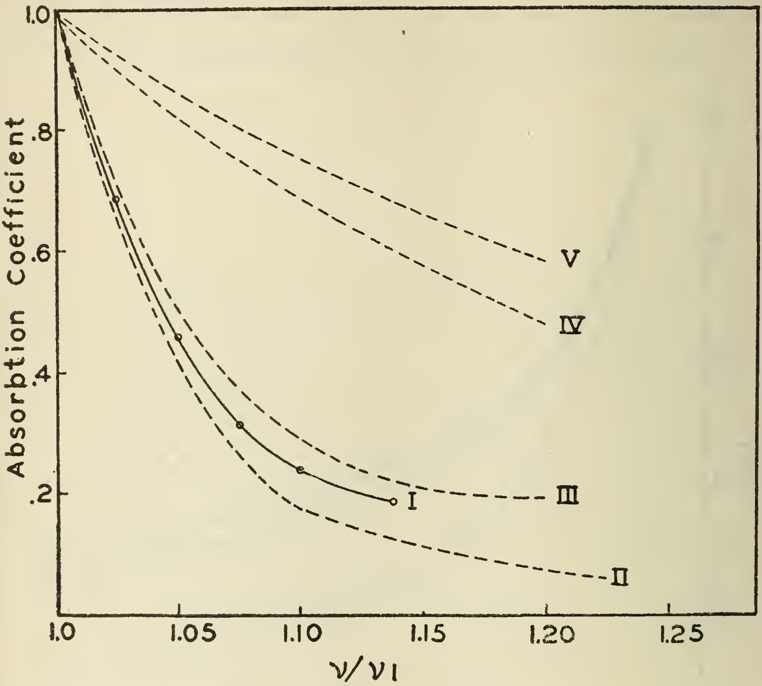

FIGURE 4.—*Relative photo-electric absorption coefficients*-

N is the frequency of the light; N(*l*) the frequency of the series limit.
Curve *I*, *K* for the caesium 1^2S level deduced from recombination probabilities.
Curve *II*, same quantity from direct measurements of Lawrence and Edlefesn.
Curve *III*, same quantity from direct measurements of Mohler and Boeckner.
Curve *IV*, *K* for the 2^2P and 3^2D caesium levels from recombination measurements.
Curve *V*, *K* for the continuous X-ray absorption spectrum. (Similar to the theortetical curve for a hydrogen atom.)

The absorption coefficient (K) in the region of photo-electric absorption deduced from (4) is shown in curve *I*, Figure 4. Curves *III* and *II* are taken from the direct measurements of the same quantity by Mohler and Boeckner, and Lawrence and Edlefsen, respectively. Curve *I* was obtained by computing a complete curve from each of three plates, each plate containing two or more exposures from the caesium discharge and several comparison exposures, and averaging the ordinates of the curves. The average deviation of the separate curves from the mean was 12 per cent. The absorption curve of Figure 2 is regarded as agreeing with either of the directly determined curves within the possible experimental error. It may

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[12] Mohler, Foote, and Chenault, Phys. Rev., 28, p. 37; 1926.

be remarked that the absorption probabilities for sodium, obtained by Trumpy[13] from direct absorption measurements, also agree with the caesium results.

IV. CONCLUSION

The results obtained afford additional evidence that the method of obtaining recombination probabilities is sound and that the probe wire measurements give correctly the electron velocity distribution in a discharge. Evidence is also given as to the truth of the principle of detailed balance in so far as it applies to the two inverse processes of photoionization and recombination.

V. NOTE ON THE POTASSIUM 1^2S RECOMBINATION SPECTRUM

Lawrence[14] has shown that the photo-electric absorption in potassium has a maximum at the series limit 2,859 A, falls to a minimum and then rises to a much higher maximum at 2,300 A. The recombination probability as a function of the electron velocities should, therefore, show a like anomalous behavior. Measurements similar to the above were made of the potassium recombination spectrum to check this point. Owing, apparently to the high electron temperature, the 2^2P continuous spectrum completely overshadowed the 1^2S and made any measurements impossible. A plot of the intensity similar to Figure 2 showed an unbroken straight line with no discontinuity at the 1^2S limit as in caesium.

WASHINGTON, November 21, 1930.

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[13] Trumpy, Zeit. f. Physik., **54**, p. 372; 1929.

[14] Lawrence and Edlefsen, Phys. Rev., **34**, p. 1056; 1929.

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